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BIOMATERIALS

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FORMATION OF GLASS-CERAMIC COATINGS ON BIOINERT SUBSTRATES

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A method has been developed for forming glass-ceramic coatings on bioinert substrates directly from an organic solution, making it possible to create on porous materials thin bioactive layers replicating the form of the carrier pores. The method of obtaining from organic solutions bioglasses with different composition has advantages over the use of water solutions by avoiding fractional crystallization during evaporation and over the sol-gel method by penetrating more easily into the pores in bioinert carriers and forming multilayer coatings.

Key words: bioinert ceramic, bioglass, bioactive coatings.

One of the most rapidly developing directions of modern medical materials engineering is the development of implants for replacing damaged bone tissue. At present metals and alloys as well as polymer and ceramic materials are finding applications for fabricating bone prostheses in reconstructive bone surgery.

Regenerative materials capable of restoring the structural and functional integrity of bone tissues by stimulating the osteogenic cells of the bone itself and activating their synthetic and secretory capacity are widely used. Cements based on calcium phosphates are among a large number of materials that have been proposed as promising bone substitutes since their structure is similar to that of bone tissue [1]. Such cements are bioactive and fuse well with bone, gradually dissolving and regenerating the bone tissue.

Biodegradable phosphate and silicate glasses are finding practical applications. For example, glass powders with the composition (mol.%) 45 P_2O_5, 50 CaO and 5 Al_2O_3 with boron, titanium and zirconium oxides added are used in making implants based on calcium phosphate glass-ceramic materials [2]. Burnable additives such as starch, graphite rods, capron and lavsan thread, gelatin, carbamide, paraffin and others are used as pore-forming agents [3]. Because their chemical and mineralogical compositions are close to that of bones bioglasses are compatible with the physiological medium in humans.

A significant drawback of cements and bioglasses is that their mechanical properties are inferior to those of bone tissue (low tensile strength, low impact resistance, brittleness and others). This makes them unsuitable for use in implants for load-carrying bones. For this reason a more promising direction is to use stronger materials, for example, titanium materials [4], for bioactive glass-ceramic coatings on load carriers.

Ceramic based on Al_2O_3 is attractive as a material for implants because it is strong and chemically inert. However, it has a significant drawback: because mechanical loads are screened the bone tissue adjoining the implant is gradually resorbed. This is associated with the fact that the physical-chemical and mechanical properties of the implant are different from those of the bone tissue. Nevertheless, at present there are no alternatives to such materials, for example, as replacements for hip joints. The development of a transitional zone between bone and implant that could impart long-time stability to the implant is one solution to the present situation. Osseointegration, which presupposes an anatomical interconnection of the changing live bone and the surface of the implant, could provide such stability.

In summary, biocompatible coatings that stimulate tissue regeneration and do not adversely affect the living organism must be deposited on bioinert ceramic implants. The ceramic substrate imparts the required strength while the coating provides high biocompatibility. It is assumed that after some time the bioactive layer will dissolve completely or partially and the implant itself will form a strong bond with the bone. Hydroxyapatite (HAP) and bioactive glasses are such bio-

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active materials [5, 6]. HAP ($Ca_{10}(PO_4)_6(OH)_2$) is an inorganic component of the bone matrix with the stoichiometric calcium-to-phosphorus ratio Ca/P = 1.67. This explains the high biocompatibility of this material. Among bioactive glasses the one most actively used is the composition 45S5 with the following molar content (mol.%): 24.5 Na_2O, 24.5 CaO, 45 SiO_2 and 6 P_2O_5. The bioactivity and resorbability of glasses can be changed by varying the composition [7].

A number of methods are now being used to form such coatings: magnetronic deposition, sol-gel method, vapor deposition and ion-plasma deposition [8 – 11]. The authors are of the opinion that the most convenient method, which does not require the use of complicated expensive equipment, is the formation of glass-ceramic coatings on bioinert substrates directly from solution.

The aim of the present work was to investigate the possibility of forming glass-ceramic coatings on bioinert substrates directly from solution, which makes it possible to obtain coatings that replicate the surface relief of the implant.

EXPERIMENTAL PART

Sample A. Using a spatula kaolin powder and water (mass ratio S : L = 2 : 1) were mixed on glass to a uniform state. The mixture was placed into a 1 × 1 × 0.6 cm mold and dried at room temperature in 1 day. Next the sample was removed from the mold and fired in a muffle furnace to temperature 700°C with heating rate 10 K/min.

Sample B. The kaolin and hydroxyapatite (HAP) powders were mixed in the mass ratio 3 : 1 and then combined with water (ratio S : L = 2 : 1). The sample formed was obtained similarly to the sample A. The HAP for this sample was obtained as follows. Calcium acetate $Ca(C_2H_3O_2) \cdot H_2O$ was mixed with oleic acid $C_{18}H_{34}O_2$ in the molar ratio 1 : 2. The mixture was heated at temperature 200°C until the calcium acetate dissolved completely. Then a benzene solution of tributyl phosphate (TBP) in the molar ratio Ca : TBP = 1.67 : 1 was added. This mixture was heated for 1 h at 200°C, fired in a muffle furnace at 700°C at heating rate 10 K/min and allowed to cool inside the furnace to room temperature.

Sample C. The ceramic sample was obtained by ultrasonic gas-dynamic deposition of aluminum oxide onto a metal mesh [12, 13]. X-ray phase analysis showed the following phases to be present in the ceramic: α-Al_2O_3 (corundum), the cubic modification of γ-Al_2O_3 ($a = b = c = 7.924$ Å) and the tetragonal modification of δ-Al_2O_3 ($a = b = 7.943$ Å, $c = 23.5$ Å).

Sample D: Porous ceramic from γ-Al_2O_3 (TU 2163-015-44912618–2003).

Solutions containing tetraethoxysilane, tributyl phosphate, sodium oleate and calcium oleate in an organic solvent (turpentine) were used as the precursor to obtain bioglass with the composition (%): 11.0 Si, 14.9 Ca, 5.1 P, 14.8 Na, 9.2 C and 45.0 O. A bioglass coating was formed on the ceramic by permeation into the sample followed by firing in a muffle furnace at 1200°C with heating rate 15 K/min.

A D8 ADVANCE diffractometer was used to obtain diffraction patterns of the samples in CuK_α radiation (graphite monochromator). X-ray phase analysis with the EVA software and PDF-2 powder data bank was used to monitor the composition of the powders. Scanning electron microscopy (SEM) with the Hitachi S5500 SEM was used to study the morphology of the samples. An ASAP 2020 analyzer and sorption of nitrogen at liquid-nitrogen temperature were used to determine the specific surface area and the pore size and volume. The thermal aging temperature was 300°C. The specific surface of the samples was determined by the BET method and the pore size and volume by the BJH method.

RESULTS AND DISCUSSION

As noted above bioactive glass-ceramic coatings on carriers made of stronger materials are used for implants as replacements for bone tissue. The most convenient method of obtaining coatings without the use of complicated expensive equipment is permeation into porous carriers followed by firing. Batch containing the components of the glass can be used for this. In the last few years the sol-gel methods used both to obtain hydroxyapatite powder as well as for bioglasses have seen the greatest development [14 – 16]. At the same time the preparation of sol from the initial reagents, such as tetraethoxysilane, calcium nitrate, sodium nitrate, triethylphosphate and nitric acid, requires 5 days, i.e., this is a quite long process. The authors are of the opinion that it is more convenient to use as a precursor solutions containing tetraethoxysilane, tributyl phosphate, sodium oleate and calcium oleate in an organic solvent, for example, turpentine, to obtain bioglasses. Such solutions, in contrast to batches or sols, easily penetrate into any pores and on firing form thin films replicating the form of the pores in the bioinert carrier.

Photomicrographs and the energy dispersion spectrum of a fragment of the glass obtained from a solution containing tetraethoxysilane and sodium and calcium oleates in turpentine are presented in Fig. 1. The composition of the glass is as follows (%): 11.0 Si, 14.9 Ca, 5.1 P, 14.8 Na, 9.2 C and 45 O (Ca/P = 2.28).

The permeation of the organic solution into the porous sample D, whose SEM image and energy dispersion spectrum are presented in Fig. 2, as well as the subsequent firing of the sample at 1200°C, showed the following: a thin layer of bioglass does not destroy the micro geometry of the surface (Fig. 3*a*); calcium, phosphorus and sodium lines appear in the energy dispersion spectrum; and, the aluminum line practically vanished (Fig. 3*b*).

The main implant characteristics allowing endoprostheses to be secured in bone tissue and, as a result, to have durability and functionality are texture and surface properties. Implants with a developed microrelief give better clinical outcomes compared with smooth implants. The experi-

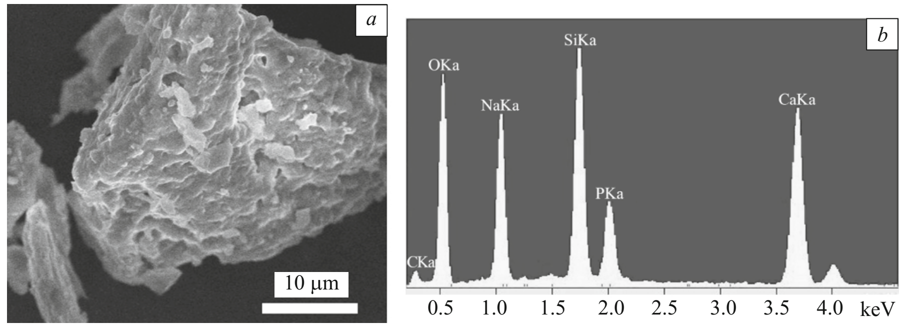

Fig. 1. Bioglass: *a*) SEM image; *b*) energy dispersion spectrum.

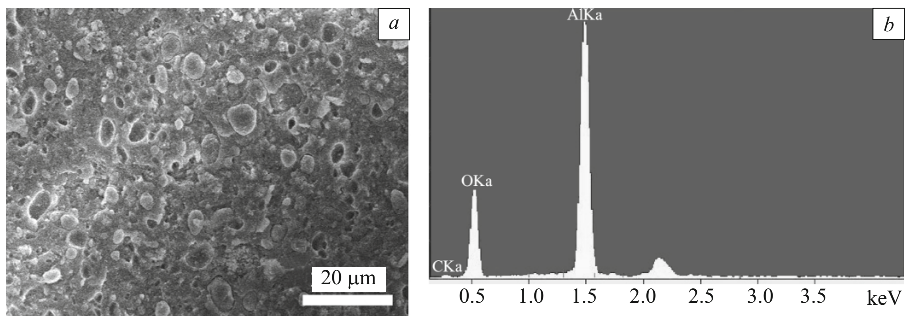

Fig. 2. Sample D: *a*) SEM image; *b*) energy dispersion spectrum.

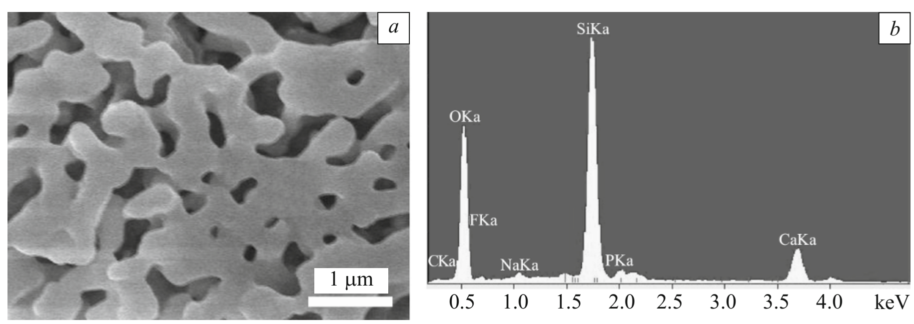

Fig. 3. Sample D with a bioglass coating: *a*) SEM image; *b*) energy dispersion spectrum.

mental studies indicate that the micro geometry of a surface with 1 – 10 μm asperities gives the best adhesion between embryonic bone tissue and the surface of an implant. And the presence of hemispherical pores ranging in depth from 1.5 to 4 μm is optimal for osseointegration [17, 18]. In this connection it is very important to develop a method of forming coatings on porous carriers replicating the form of their pores.

The characteristics of the samples A, B, and C were studied in the course of this work. The morphology of a fracture surface of sample A is characterized by the presence of pores with sizes 0.5 – 2 μm and 10 – 20 μm (Fig. 4*a*). As result of the permeation of an organic solution into this ceramic and firing at 1200°C a thin film of bioglass replicating the form of the pores in the bioinert carrier is formed. An advantage of the method proposed for forming coatings is that it can be used to obtain multilayer coatings (Fig. 4*b*), which will make it possible to satisfy the medical and technical specifications for coatings on implants for surgery. The thickness of the final biocoating on an implant can be changed by varying the number of layers.

The porosity of the kaolin sample decreases with increasing firing temperature. However, a very small decrease of the porosity elicits a two-fold increase of the strength under compression (Table 1, samples 1 and 2). Adding HAP pow-

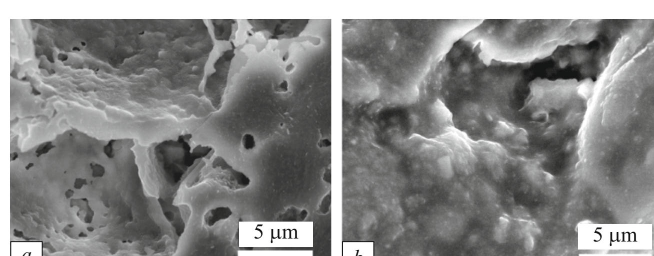

Fig. 4. Sample A: *a*) initial sample; *b*) sample coated with three layers of bioglass.

TABLE 1. Characteristics of Samples with Different Compositions

Sample No.	Sample	Firing temperature, °C	Strength under compression, MPa	Specific surface, m^2/g	Pore volume, cm^3/g	Pore size, nm
1	A	700	26.11	12.75	0.0770	26.52
2	A	1200	53.13	3.330	0.0167	21.42
3	A + bioglass	1200	60.00	0.795	0.0015	12.06
4	B	700	14.00	8.355	0.0540	29.23
5	B	1200	37.50	1.007	0.0025	38.41
6	B + bioglass	1200	42.80	1.300	0.0021	16.52
7	C	1200	223.10	0.270	0.0015	17.47
8	C + bioglass	1200	278.50	0.260	0.0015	21.80

der to the kaolin in an amount equal to one-third the mass of the kaolin decreases the strength of the sample two-fold (samples 1 and 4). An increase in the firing temperature results in an increase of the porosity of the material, probably because the HAP decomposes at temperatures above 800°C [4]. Nevertheless, the strength of the sample increases more than 2.5-fold (samples 4 and 5).

The experimental samples have macropores of size 0.5 – 20 μm and micropores. The volume and average size of the micropores are presented in Table 1.

The bioglass coating on the initial samples increases their strength appreciably (samples 2 and 3, 5 and 6, and 7 and 8).

Unfortunately, none of the kaolin samples possesses sufficient strength for use in implants. An implant with appropriate mechanical properties must be used to replace defective bone, and medical research shows that the strength of cortical bone tissue is of the order of 100 – 230 MPa [19].

The ceramic C is much more appropriate in this respect. Its strength is comparable to that of human bone tissue (see Table 1). In addition, this ceramic is characterized by a developed microrelief (Fig. 5*a*), which is required in order for the embryonic bone tissue to adhere to the implant surface itself. The size of the asperities fluctuates from 1 to 10 μm. As indicated above this range gives the maximum adhesion between the implant and the bone tissue. Coating this ceramic with an organic solution and firing at 1200°C yields a continuous bioglass film (Fig. 5*b*).

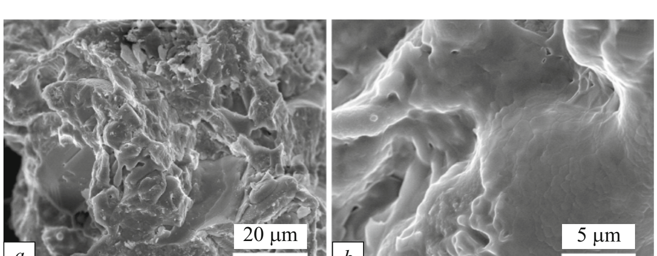

Fig. 5. Sample C: *a*) initial sample; *b*) sample coated with three layers of bioglass.

CONCLUSIONS

A method has been developed for forming glass-ceramic coatings directly from an organic solution on bioinert substrates. This method makes it possible to create on porous materials thin bioactive layers replicating the form of the pores in the carrier. The method of obtaining bioglasses with different composition by using organic solutions has advantages, on the one hand, over methods using water solutions because fractional crystallization during evaporation can be avoided and, on the other hand, over sol-gel methods because true solutions more easily penetrate into the pores of bioinert carriers.

In addition, the method makes it possible to form multilayer coatings, which will make it possible to meet the medical and technical specifications for coatings on implants for surgery. The thickness of the final biocoating on an implant can be changed by varying the number of layers.

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